

magnitude, whereas the "saline" ionisation does not. Taken in conjunction with the electric conductivity, the cryoscopic method should yield results of utility with soluble electrolytes whose ionisation is considerable. As a means of determining the extent to which acidic or basic ionisation, as distinguished from saline ionisation, has taken place, measurements of electromotive force with hydrogen electrodes may, in some instances, be applied with success. Experiments in this direction are at present in progress.

"The Electrical Conductivity and other Properties of Sodium Hydroxide in Aqueous Solution, as elucidating the Mechanism of Conduction." By WILLIAM ROBERT BOUSFIELD, M.A., K.C., M.P., and THOMAS MARTIN LOWRY, D.Sc., Lecturer in Physical Chemistry and Crystallography at the Central Technical College. Communicated by Professor H. E. ARMSTRONG, F.R.S. Received June 24,—Read November 17, 1904.

(Abstract.)

The original object of the research was to investigate the decay, as the temperature rises, in the "ionising" properties of water; which is manifest, especially in the case of the alkalies, in the inflected character of the curves expressing the relation between temperature and conductivity in aqueous solutions.* It was found, however, that the available data for the physical properties generally of the alkalies were very few; the inquiry was, therefore, extended so as to include the measurement of the density and conductivity of solutions of sodium hydroxide at 18° C., as well as of the temperature co-efficients of conductivity and density. The great viscosity of the more concentrated solutions being very noticeable, measurements of viscosity were also made, in order to correlate this property with the low conductivity of these solutions. The principal results of the investigation are as follows:—

(1) In the most dilute solutions, in which "ionisation" is nearly complete, the curves expressing the relation between molecular conductivity and temperature are not inflected between 5° and 100° C. They resemble the curves representing the changes in viscosity with temperature in dilute aqueous solutions. Concentrated solutions also give curves that are not inflected. In these solutions a very rapid increase of conductivity takes place as the temperature is raised: the conductivity of a 50-per-cent. solution

* Compare 'Roy. Soc. Proc.,' 1902, vol. 71, pp. 42—54.

increasing 5-fold between 0° and 18° and 80-fold between 0° and 100° C.; the form of the conductivity-temperature curves again appears to be determined mainly by molecular changes rendered apparent in the rapid changes of viscosity which accompany changes of temperature. Moderately dilute solutions give curves that are inflected between 0° and 100°; a regular curve can be drawn connecting the temperature of inflection with the percentage of sodium hydroxide in the solution: this temperature reaches a minimum, at 48° C., in the case of a normal (4 per cent.), solution, but rises to 100° C. when the concentration is raised to 30 per cent.

(2) The inflected conductivity-temperature curves can be represented by the simple cubic formula

$$\kappa_t = \kappa_0 + \alpha t + \gamma (t - \tau)^3,$$

where τ is the temperature of inflection. As this formula is unsatisfactory when applied to curves that are not inflected between 0° and 100° C., a formula was devised which was based upon the three factors of concentration, ionisation and ionic mobility, on which the variations of specific conductivity depend. The influence of temperature on the density, and therefore on the concentration, has been experimentally determined and can be directly allowed for; in order to express the influence of temperature on the other two factors, it has been assumed that the variation of ionic mobility with temperature may be expressed by a formula similar to that of Slotte for the variation of fluidity

$$\eta_0/\eta = (1 + bt)^n,$$

and that the decay of ionisation with rising temperature may be expressed by a formula similar to that of Abegg and Seitz for the decrease in the dielectric constant

$$D/D_0 = e^{-at}.$$

The formula $\frac{\kappa_t}{\kappa_0} = \frac{\rho_v}{\rho_0} (1 + bt)^n e^{-at}$, which has been used to express the influence of temperature on conductivity, has the advantages that it is applicable to conductivity-temperature curves of all kinds, that a definite physical meaning can be given to each of the constants, and that it gives expression, not only to the inflection now under consideration, but also to the maximum conductivity and the second inflection in the general conductivity-temperature curve.* What is, perhaps, of even greater importance, is the fact that it has been found possible, with the help of this formula, to make some approximation to resolving the two opposing influences which determine the form of this curve.

(3) The density tables for caustic soda, in general use until about 10 years ago, were based on the early measurements of Dalton and of

* *Loc. cit.*, p. 52.

Tünnermann (1827). A revised table was published by Hager in 1883, but the first table in which even the second place of decimals is correctly given is that of Pickering (1894). Pickering's solutions were prepared from purified material, but were standardised by titration, and can therefore be relied on only to the third place of decimals. The re-determination of the densities was undertaken in order to obtain a method of standardisation that should be more accurate than titration. Quantities of sodium, amounting to about 150 grammes at a time, were weighed, and converted quantitatively into concentrated solutions of sodium hydroxide by the action of steam in a platinum vessel. Eleven determinations, made with six different standard solutions, gave, as the density of a 50-per-cent. solution, the value 1.5268, with an average error of 0.0001. Solutions of known concentrations having been prepared by dilution, their densities were determined; it was then possible, by measuring the density, to determine the percentage of sodium hydroxide in any pure solution, with an error only one-tenth as great as that introduced in standardising by titration. This method contributed greatly to the accuracy of the electrical measurements; in the absence of such a method, the measurements of some of the earlier investigators have been vitiated by errors in the concentration, amounting to as much as 2 per cent. on the total weight of alkali in the solution.

(4) The determination of the conductivity at 18° C. of solutions prepared in this way led to results which, although slightly different from the earlier observations of Kohlrausch, gave a curve of similar form. The maximum conductivity at 18° C. is 0.3490 in a 15-per-cent. solution, the value given by Kohlrausch being 0.3462. At higher temperatures the maximum conductivity is considerably greater, rising to over 1.4 at 100°, and occurs in solutions of greater concentration.

(5) The viscosity of a 50-per-cent. solution of sodium hydroxide is approximately seventy times as great as that of water. This increase of viscosity must produce a large effect on the ionic mobility; the influence of this factor may be to some extent eliminated by dividing the molecular conductivity by the fluidity, and this ratio we have called the "intrinsic conductivity" of the solution. Whilst the molecular conductivity of sodium hydroxide solutions decreases steadily as the concentration is increased, the intrinsic conductivity falls to a minimum at about 8 per cent. NaOH, and then rises, until at 50 per cent. NaOH, the value is considerably greater than in the most dilute solutions. It is believed that this increase is due to the fact that liquid soda is an electrolyte, *per se*, and that, in concentrated solutions, the current is conveyed partly by the soda alone, as if it were in the fused state.

(6) A study of the influence of temperature on the density revealed the fact that the addition of soda produces a simplification in behaviour

that may be attributed to the destruction by the soda of the ice-molecules present in the water. In the formula

$$\rho_t = \rho_0 + \alpha t + \beta t^2 + \gamma t^3,$$

which represents the influence of temperature on the density of water and aqueous solutions of soda, the coefficient of t^3 vanishes when a concentration of 12 per cent. NaOH is reached, whilst the coefficient of t^2 vanishes at 42 per cent. NaOH; at the latter concentration there is a simple linear relationship between density and temperature.

(7) The molecular volume of sodium hydroxide in dilute aqueous solution has a large negative value, a litre of water dissolving 140 grammes of sodium hydroxide at 0°, 100 grammes at 18°, or 60 grammes at 50°, without increasing in volume. It is noteworthy that the molecular volume does not increase continuously as the temperature rises, but reaches a maximum value at about 70° C. In a 50-per-cent. solution, however, the temperature has little effect on the molecular volume, the extreme variation being only about 10 per cent.

“The Refractive Indices of the Elements.” By CLIVE CUTHBERTSON.
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(Abstract.)

In a letter addressed to ‘Nature,’ in October, 1902, attention was drawn to the fact that the refractivities of the five inert gases of the atmosphere, He, Ne, A, Kr, and X, as determined by Ramsay and Travers, were, within narrow limits of accuracy, in the proportion of 1, 2, 8, 12 and 20; or, more simply, of $\frac{1}{4}$, $\frac{1}{2}$, 2, 3, and 5.

In a second letter it was shown that the refractivities of the halogens, Cl, Br, and I, stand also in the relation of 2, 3, and 5 to the same degree of accuracy; but it was pointed out that the figures for P, As, and S, as measured by M. Le Roux in 1861, did not show any similar relation; and it was observed that a redetermination of them would be interesting.

With a Jamin’s refractometer, adapted for use with high temperatures, results have now been obtained for Hg, P, and S, which differ widely from those of M. Le Roux. The index of mercury, calculated for a molecule containing two atoms, is placed at 1·001857, a number which agrees closely with the value given by the refractive equivalent of Gladstone. The index of P₂ is found to be 1·001197 and that of S₂ is 1·001101.

In all three cases it is estimated that the margin of error does not